

MIGRATION OF SULFUR BETWEEN ORGANIC AND INORGANIC PHASES DURING HYDRODESULFURIZATION PROCESSES¹

Lois V. Dunkerton*², Keith C. Hackley³, John B. Phillips², Somenath Mitra², Sanjiv Mehrotra², and Asutosh Nigam²

Department of Chemistry and Biochemistry, Southern Illinois University at Carbondale, Carbondale, Illinois 62901, and
Illinois State Geological Survey, 615 E. Peabody Drive, Champaign, Illinois 61820

The co-occurrence of organic sulfur and iron sulfides in high-sulfur coal and their interrelationships are suggested to play an important role in the design and effectiveness of methods for precombustion desulfurization. The mobility and interconversion of pyritic and organic sulfur forms can be both advantageous as well as disadvantageous. Iron catalysts have been reported to exhibit high activity in coal gasification (4). More extensive studies have been done regarding the role of iron sulfides in hydroliquefaction in which pyrite is transformed to pyrrhotite and H₂S which will catalyze hydroliquefaction around 380°C (5). Studying this phenomena in more detail, with coal model compounds, showed that 316 stainless steel was a radical scavenger in the H₂S promoted radical chain cleavage of the model compounds, while pyrrhotite and pyrite decreased the reaction rate to a lesser extent (6-9). The formation of sulfur-containing organic compounds during hydrogen sulfide promoted liquefaction leading to reduction of overall desulfurization is undesirable. This is especially disadvantageous if either inorganic sulfur or easily desulfurized organic sulfur compounds are converted to less easily desulfurized thiophenic sulfur. The identification of organosulfur compounds in coal using reductive, oxidative, or metallic reagents continues to be studied with the obvious limitations in distinguishing original coal structures from secondary products formed during reactions of organic compounds with minerals, especially during pyrolysis conditions (10-18).

In the course of investigation of the non-isothermal hydrodesulfurization of model organic sulfur compounds in a coal-like environment with and without troilite, it was found that some of the non-thiophenic sulfur from the organic compounds was absorbed by troilite (1). This observation suggested that during hydrodesulfurization the organic sulfur had migrated to the inorganic phase. As the temperature was raised, more H₂S evolved from the sample with troilite, suggesting reevolution by pyrrhotite to troilite conversion.

The purpose of this study was to use isotopic labeling to determine the mechanism of incorporation of sulfur into troilite. One possibility, as suggested by the formation of pyrrhotite confirmed by Mössbauer spectroscopy, is that the H₂S produced from the organic compound was transferred to the inorganic phase, and then as the temperature was raised, H₂S evolution occurred from the troilite. Another possibility was that a direct reaction between the troilite and the organic compound took place, forming an intermediate followed by H₂S evolution from this intermediate as the temperature was raised. The fate and H₂S evolution profile from the labeling of the mobile organic sulfur group has been studied in an effort to distinguish possible mechanisms and demonstrate the role of troilite in this process.

MATERIALS

Two ³⁴S labeled compounds 2-(thiomethyl)dibenzothiophene (2) and 4-(thiomethyl)dibenzothiophene (3) were prepared from dibenzothiophene (1) using our previously reported methods as shown in Scheme 1 (19). Compounds 2 and 3 gave spectral data in agreement with their structural assignments, including high resolution mass spectral confirmation. Compound 2 gave m/z 232.0179 for C₁₃H₁₀³²S³⁴S (calculated 232.0181) and compound 3 gave m/z 232.0140.

EXPERIMENTAL

The coal-like mixture was prepared by grinding together 8 mg of compound 2 or 3 and 60 mg of charcoal (previously degassed by heating to 680°K *in vacuo*) with or without 80 mg of troilite. The mixture was placed in a pyrex tube placed in a furnace. Hydrogen was passed through the tube at a flow of 55 mL/min while heating at 3°/min from 523°K to 700°K. The evolving gases were analyzed for the ratio of H₂³²S to H₂³⁴S as the temper-

ature was raised using a quadrupole mass spectrometer attached to a split off the gas outlet. The residue was extracted with CH_2Cl_2 to recover the organic desulfurized compound, 2- or 4-methyldibenzothiophene and the remaining residue subjected to the combustion-precipitation sequence previously reported for isotopic analysis of coal pyrolysate chars (1,20).

RESULTS AND DISCUSSION

The hydrodesulfurization of 2-(thiomethyl)dibenzothiophene(2) with and without troilite gave a total H_2S evolution profile as a function of temperature shown in Figure 1. The major process producing H_2S was the desulfurization of the thiomethyl group occurring between 523°K and 600°K while the thiophenic group began to slowly desulfurize around 725°K. In the presence of troilite, the total H_2S evolution was similar, except less evolved between 523°K and 550°K, while slightly more evolved between 550°K, and 600°K. The amount of H_2^{34}S evolved from 2 is expected to follow the same profile between 523°K and 550°K. If some $^{34}\text{H}_2\text{S}$ migrated into the troilite, then at the higher temperatures, as the H_2S reevolved from the pyrrhotite, the H_2^{34}S would be diluted by isotopic mixing, resulting in decreased H_2^{34}S evolution relative to H_2^{32}S evolution. A corresponding increase in the ^{34}S isotopic composition of the char would then be expected. If no mixing occurred, the H_2^{34}S evolution profile would be expected to follow the same pattern as the total H_2S , with no increase found in the char.

REFERENCES

1. Part 2. For part 1 see Dunkerton, L. V.; Mitra, S.; Phillips, J. B.; Smith, G. V.; Hinckley, C. C.; and Wiltowska, T. *Fuel* **1988** *67*, 000.
2. Southern Illinois University.
3. Illinois State Geological Survey.
4. Ohtsuka, Y.; Tamai, Y.; and Tomita, A. *Energy and Fuels* **1987** *1*, 32-36.
5. Trehwella, M. J.; and Grint, A. *Fuel* **1987** *66*, 1315-1320.
6. Hei, R. D.; Sweeney, P. G.; and Stenberg, V.I. *Fuel* **1986** *65*, 577-585.
7. Sweeney, P.G.; Stenberg, V.I.; Hei, R. D.; and Montano, P.A. *Fuel* **1987** *66*, 532-541.
8. Yokoyama, S.; Yoshida, R.; Narita, H.; Kodaira, K.; and Markawa, Y. *Fuel* **1986** *65*, 164-170.
9. Doughty, P.W.; Harrison, G.; and Lawson, G. J. *Fuel* **1986** *65*, 937-944.
10. Boudou, J.P.; Boulegue, J.; Maléchaux, L.; Nip, M.; deLeeuw, J.W.; and Boon, J. J. *Fuel* **1987** *66*, 1558-1569.
11. Chen, P.; and Chen, W. *Fuel* **1986** *65*, 1305-1309.
12. Chakrabarity, S. K.; Iacchelli, A. *Can. J. Chem.* **1986** *64*, 861-864.
13. La Count, R. B.; Anderson, R. R.; Friedman, S.; and Blaustein, R. D. *Fuel* **1987** *66*, 909-913.
14. Clark, P. D.; Dowling, N.I.; Hyne, J. B.; and Lesage, K. L. *Fuel* **1987** *66*, 1353-1357.
15. Buchanan, A. C. III; Dunstan, T. D. J.; Douglas, E. C.; and Poutsma, M. L.; *J. Am. Chem. Soc.* **1986** *108*, 7703-7715.
16. White, C. M.; Douglas, L. J.; Perry, M. B.; Schmidt, C. E. *Energy and Fuels* **1987** *1*, 222-226.
17. Calkins, W. H. *Energy and Fuels* **1987** *1*, 59-64.
18. Johnson, D. E. *Fuel* **1987** *66*, 255-260.
19. Dunkerton, L. V.; Barot, B. C.; and Nigam, A. *J. Heterocyclic Chem.* **1987** *24*, 749-755.
20. Liu, C. L.; Hackley, K. C.; and Coleman, D. D. *Fuel* **1987** *66*, 683-688.

Scheme 1

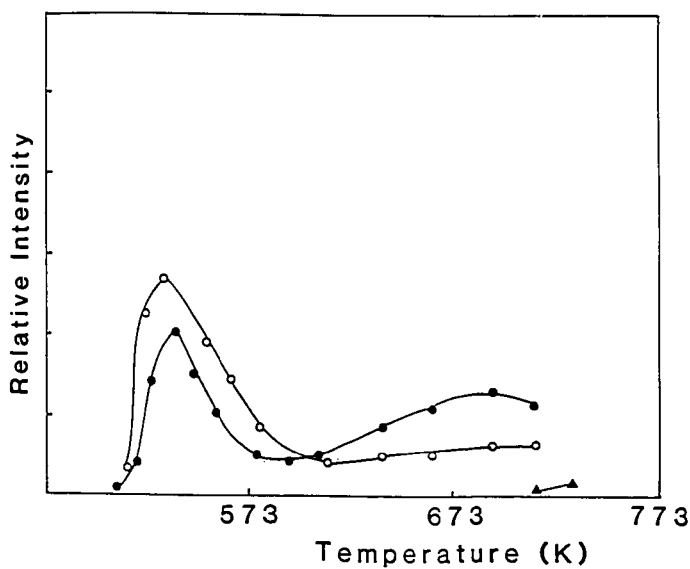
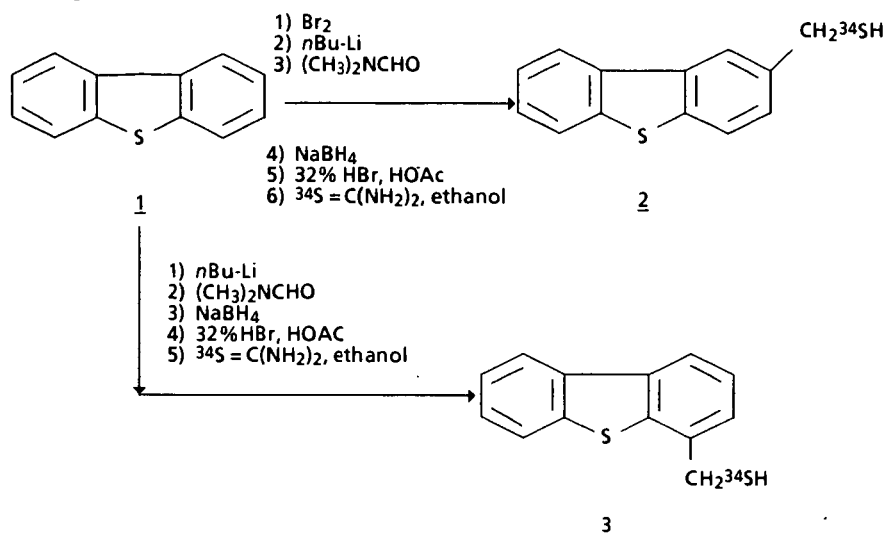


Figure 1. Rate of H_2S evolution as a function of temperature for compound 2 and dibenzothiophene at a heating rate of 3°K/min : O, compound 2 without troilite; ●, compound 2 with troilite; ▲, dibenzothiophene without troilite.